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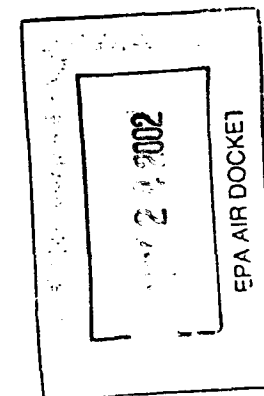
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**UNDERSTANDING THE EFFECTIVENESS OF PRECURSOR  
REDUCTIONS IN LOWERING  
8-HOUR OZONE CONCENTRATIONS**

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# Purpose of the Study

- Develop a better understanding of the physical and chemical mechanisms underlying observed ozone trends
- Assess the technical feasibility of attaining the 8-hour ozone standard



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# Key Findings

- Various VOC and NO<sub>x</sub> emissions reductions effective in reducing peak 1-hour ozone levels
- VOC reductions have modest impact on peak 8-hour ozone concentrations
- Anthropogenic NO<sub>x</sub> emissions must be reduced by 90 percent to reach the 8-hour ozone standard



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# Key Findings

- Anthropogenic VOC reductions ineffective because biogenic VOC, less reactive VOC, and CO continue to produce ozone
- Effectiveness of NO<sub>x</sub> reductions offset by an increase in ozone produced per NO
- Such NO<sub>x</sub> reductions may increase ozone levels in some areas
- These results call into question the technical feasibility of attaining the 8-hour ozone standard



# Overview of Study Approach

- Combined application of
  - analyses of ambient measured ozone data
  - photochemical modeling with process analysis
- Employ modeling to provide insights into physical and chemical processes associated with ozone formation



# Photochemical Modeling

- Choice of study area based on soundness of existing model application and availability of code with process analysis facilities
- SARMAP domain in central California
- SARMAP Air Quality Model (SAQM) with process analysis



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# Photochemical Modeling

- Extensive field measurements during summer of 1990 to support model application and evaluation
- 2-6 August 1990 ozone episode
- MM5 used to develop meteorological inputs
- Recent updates to emissions inventory by CARB



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# SAQM Emissions Sensitivity Results

- Array of VOC and NOx sensitivity runs performed by CARB using 1999 emissions
- Anthropogenic VOC and NOx emissions reduced from base case levels in 10 percent increments
- Results used to produce peak 1- and 8-hour EKMA-type isopleth diagrams



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# SAQM Emissions Sensitivity Results

- Isopleth diagrams developed using results for
  - entire study domain
  - San Jose (24 km x 24 km)
  - Stockton (36 km x 72 km)
  - Fresno (60 km x 48 km)
  - Visalia (36 km x 48 km)
  - Bakersfield (36 km x 48 km)
  - Tulare Lake (36 km x 36 km)

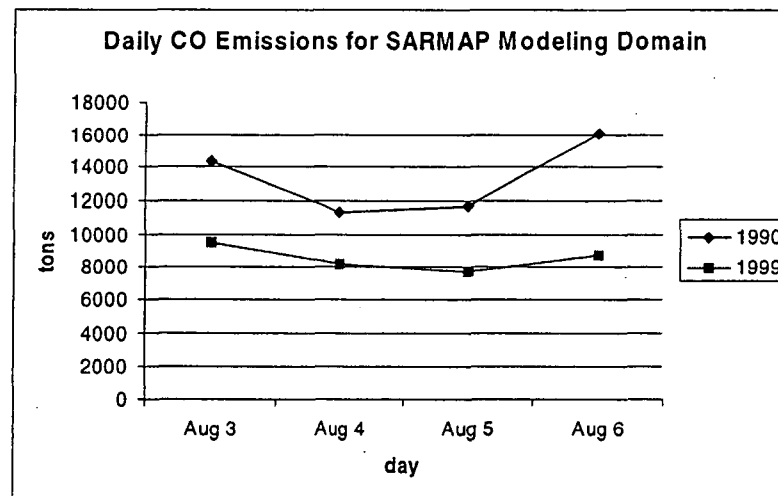
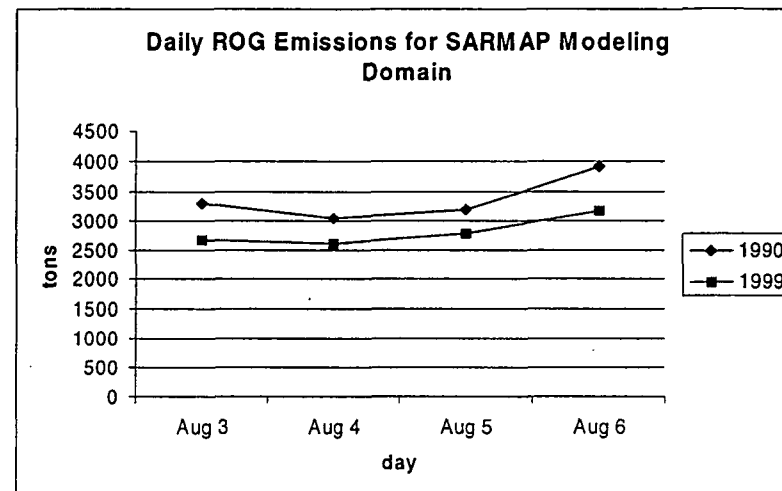
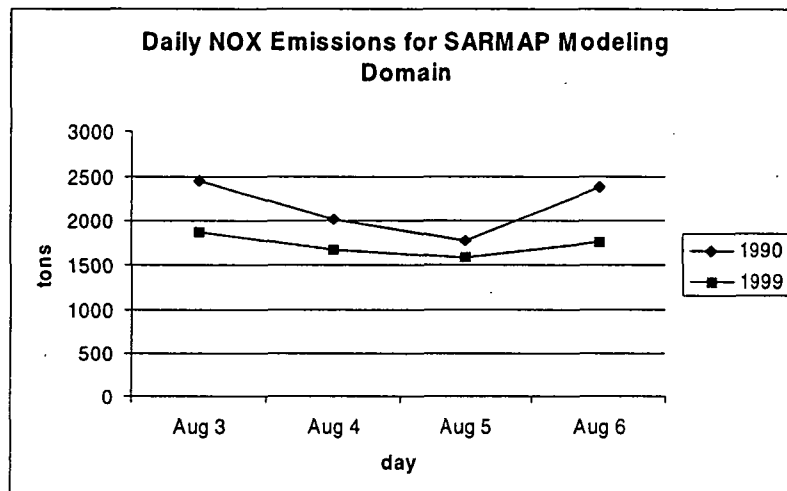


# SAQM Runs with Process Analysis

- 1990 and 1999 base case emissions
  - VOC reductions ranged from 4 to 39 percent
  - NOx reductions ranged from -7 to 41 percent
  - CO reductions ranged from 3 to 43 percent
- Additional runs with anthropogenic VOC and NOx reduced to 50 and 25 percent of 1999 base case values



# 1990 and 1999 Domain-wide Emissions



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# Percentage Change in 1999 VOC, NOx, and CO Emissions Relative to 1990 Values

Area	VOC				NOx				CO			
	Aug3	Aug4	Aug5	Aug6	Aug3	Aug4	Aug5	Aug6	Aug3	Aug4	Aug5	Aug6
	Fri	Sat	Sun	Mon	Fri	Sat	Sun	Mon	Fri	Sat	Sun	Mon
San Jose	-32	-30	-27	-31	-34	-27	-17	-32	-43	-37	-33	-43
Stockton	-25	-20	-14	-22	-32	-27	-20	-33	-37	-33	-31	-37
Fresno	-28	-20	-19	-24	-25	-15	-4	-25	-36	-29	-29	-36
Visalia	-19	-16	-7	-12	-21	-10	7	-22	-31	-26	-23	-31
Bakersfield	-39	-39	-34	-36	-40	-38	-33	-41	-40	-36	-34	-40
Tulare Lake	-19	-25	-4	-11	-20	0	9	-35	-16	-8	-3	-15



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## Model Predicted Peak Ozone Levels

- Peak 1- and 8-hour ozone isopleth diagrams for 5 and 6 August based on 1999 emissions
  - domain-wide
  - San Jose, Stockton, Fresno, Visalia, Bakersfield and Tulare Lake
- Various combinations of VOC and NO<sub>x</sub> emissions reductions effective in reducing peak 1-hour ozone



# Model Predicted Peak Ozone Levels

- VOC emissions reductions have modest impact on peak 8-hour ozone concentrations
- Anthropogenic NO<sub>x</sub> emissions must be reduced by 90 percent to reach level of 8-hour standard over entire domain



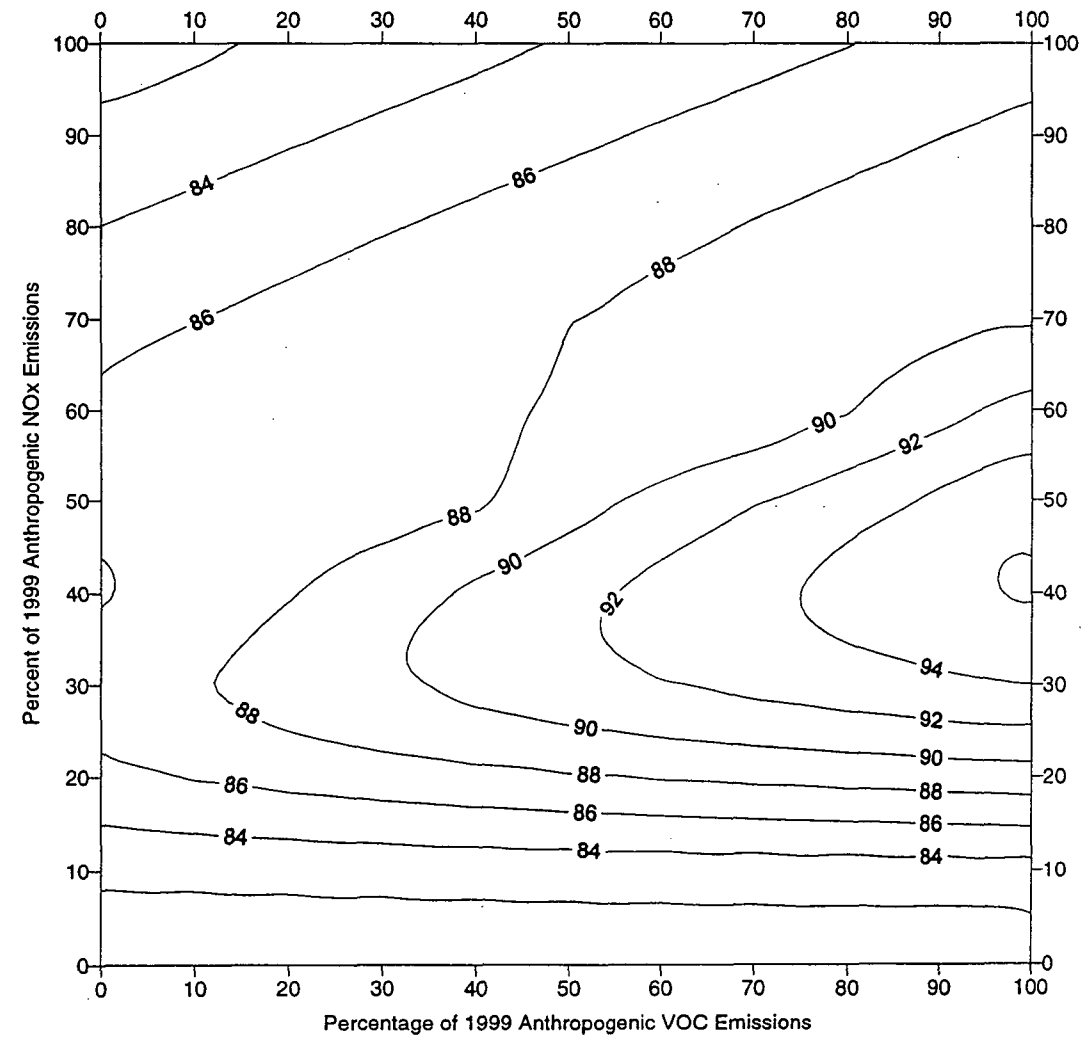
# Model Predicted Peak Ozone Levels

- With significant NO<sub>x</sub> controls, VOC reductions have small additional benefit
- Biogenic VOC emissions with small amount of anthropogenic emissions sufficient to produce peak 8-hour ozone levels at or exceeding the 8-hour standard somewhere in the domain



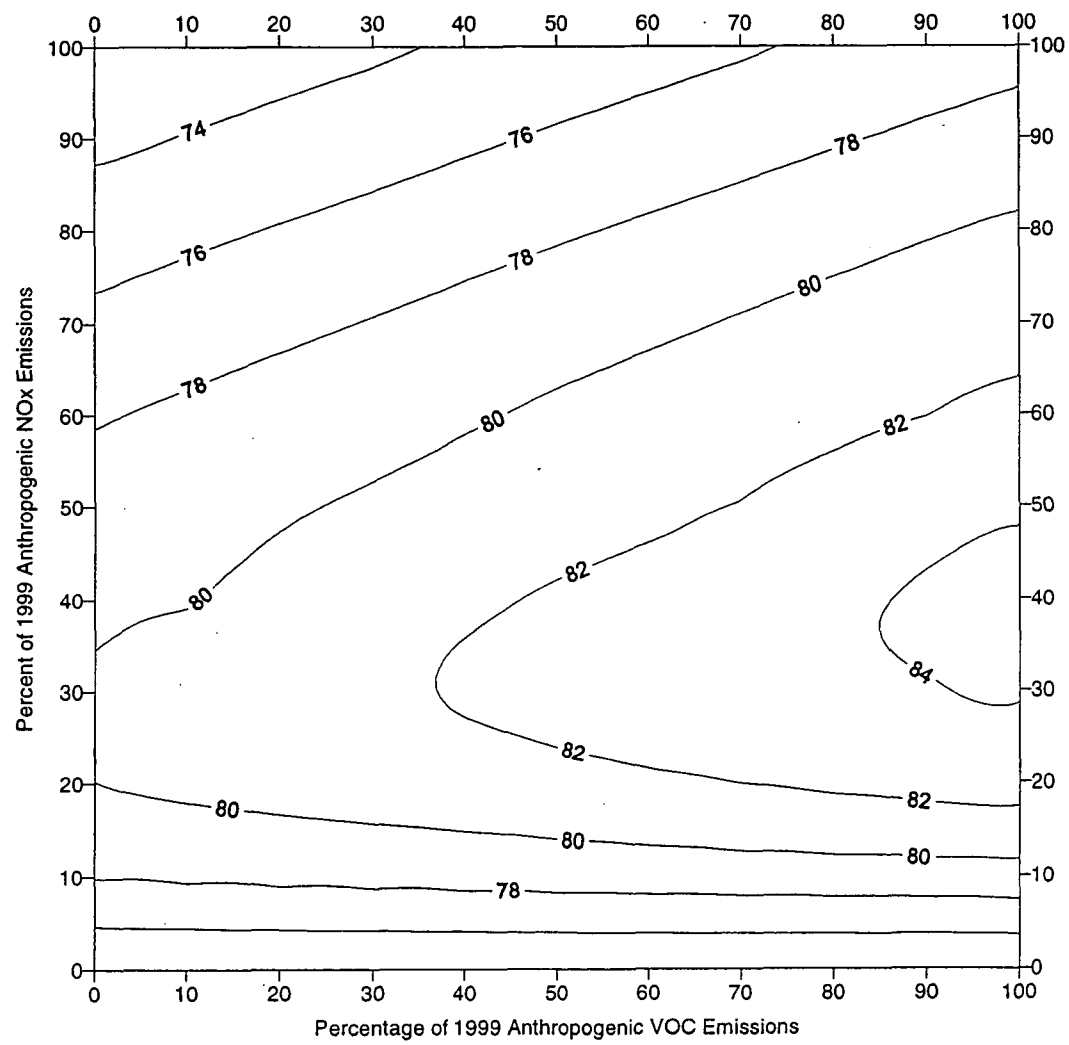


Peak 1-hour Ozone Isopleths (ppb) for San Jose Subregion - 5 August 1999



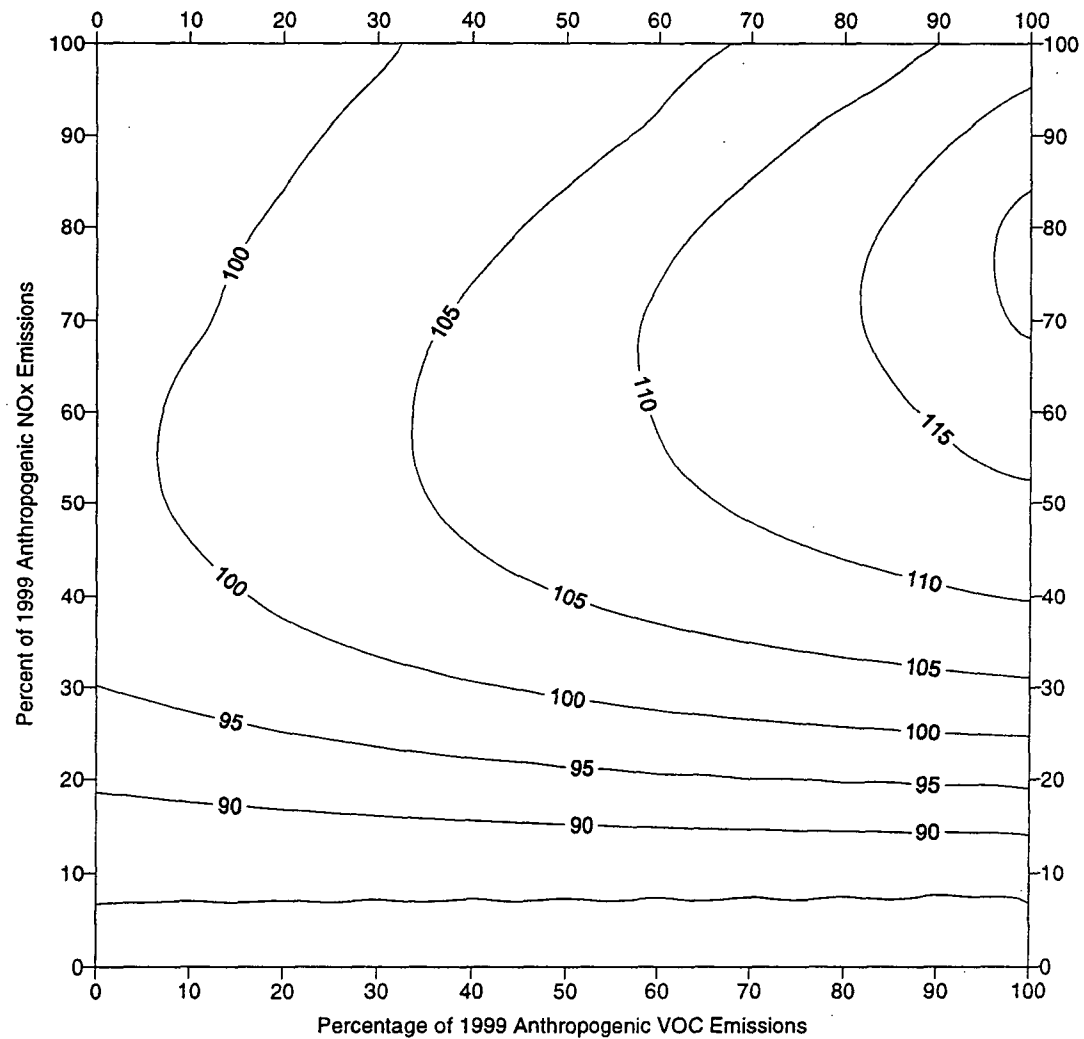
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Peak 8-hour Ozone Isopleths (ppb) for San Jose Subregion - 5 August 1999



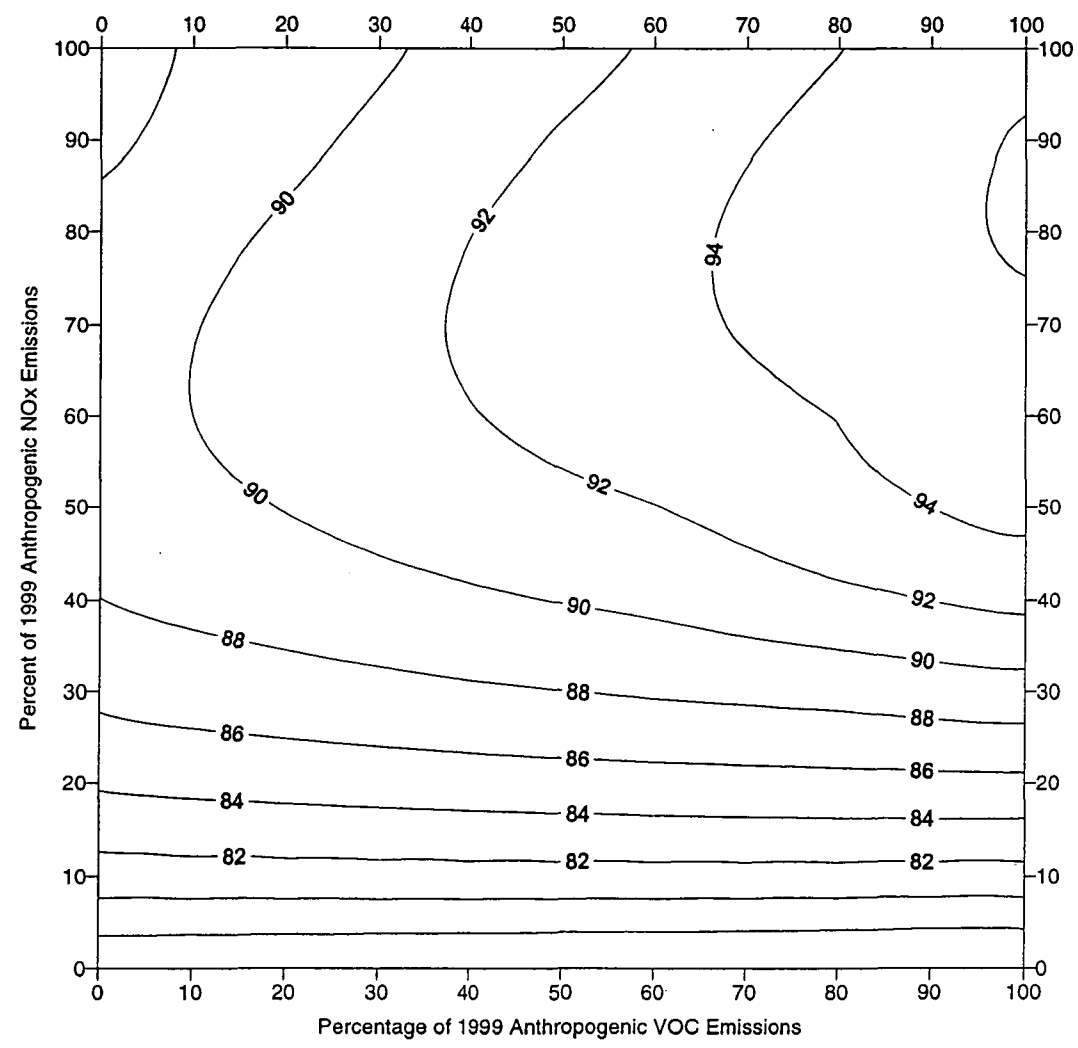
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Peak 1-hour Ozone Isopleths (ppb) for Stockton Subregion - 5 August 1999



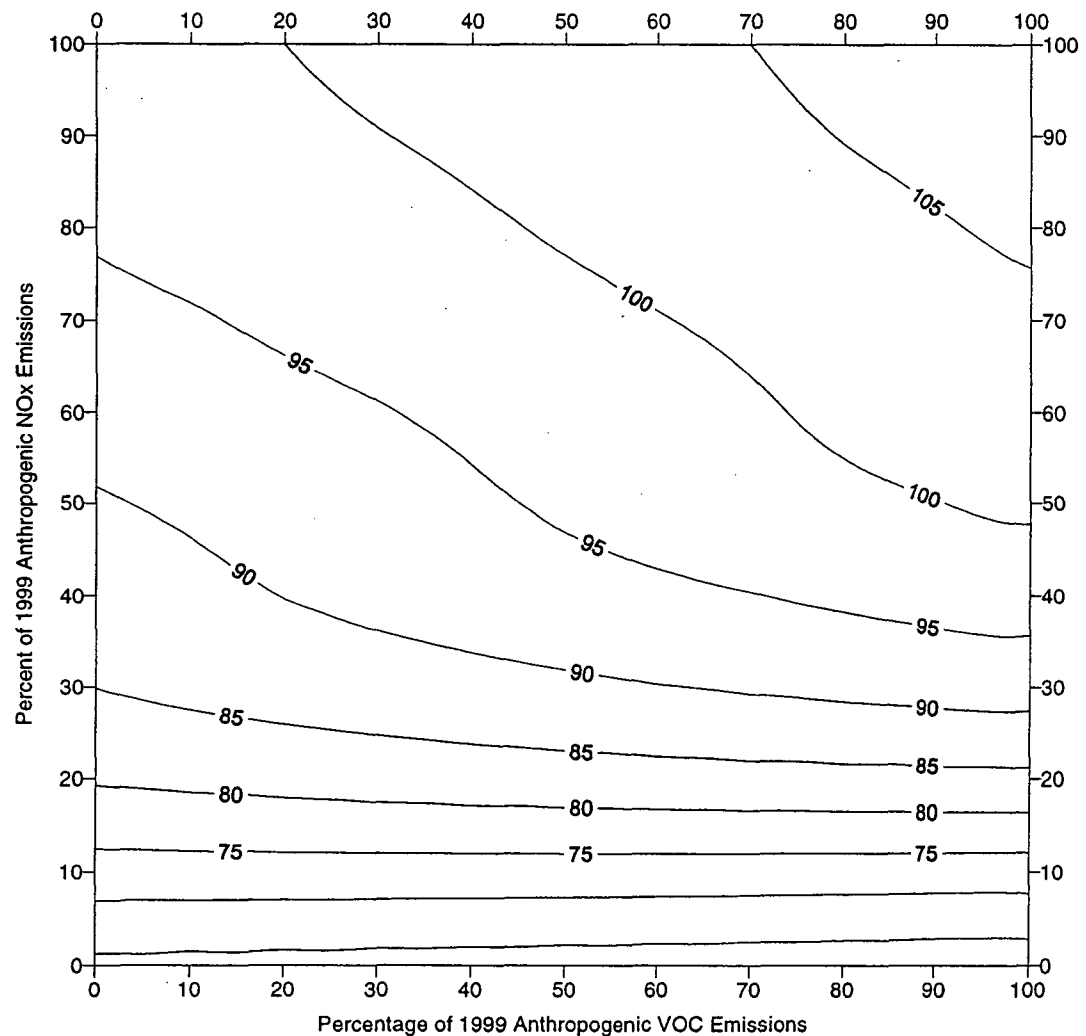
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Peak 8-hour Ozone Isopleths (ppb) for Stockton Subregion - 5 August 1999



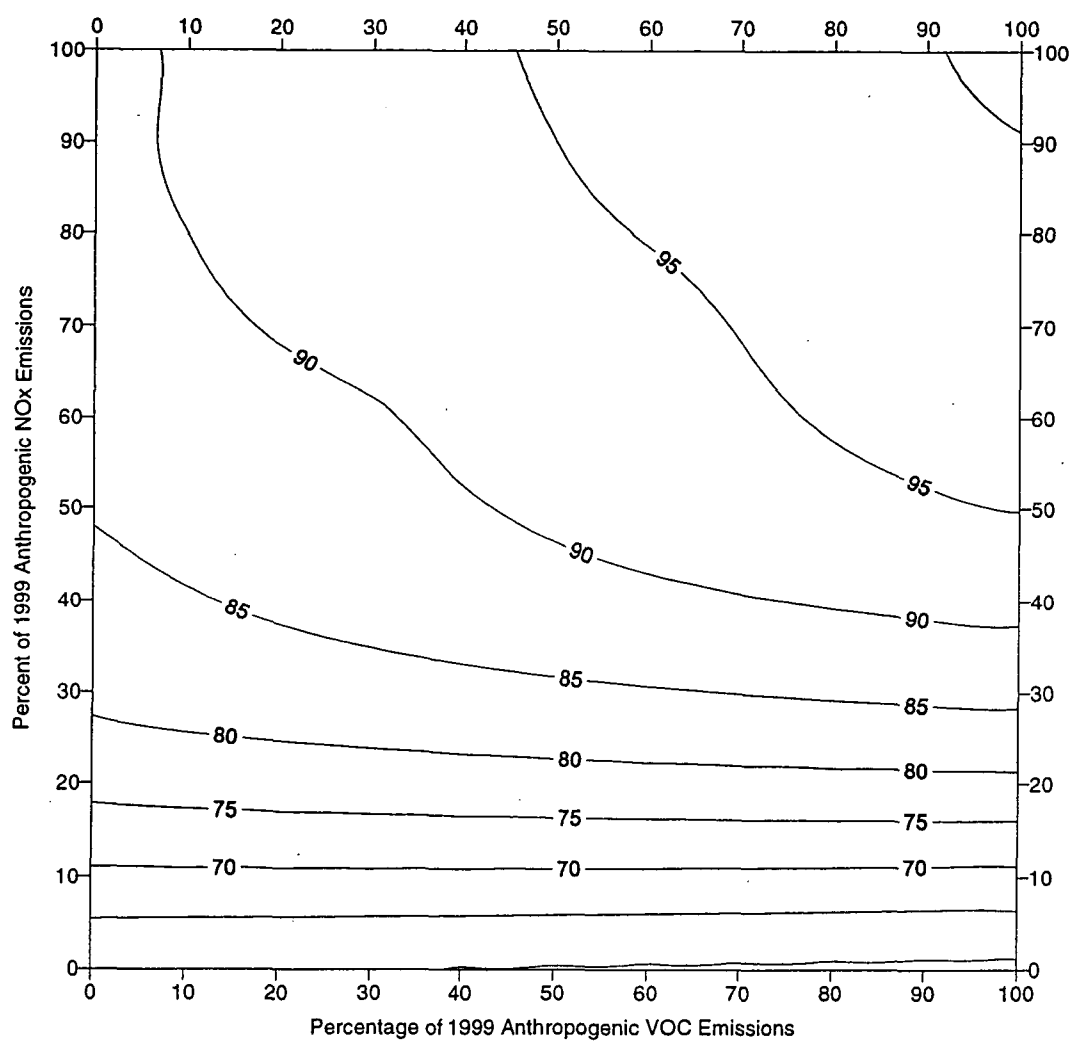
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Peak 1-hour Ozone Isopleths (ppb) for Bakersfield Subregion - 5 August 1999



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Peak 8-hour Ozone Isopleths (ppb) for Bakersfield Subregion - 5 August 1999



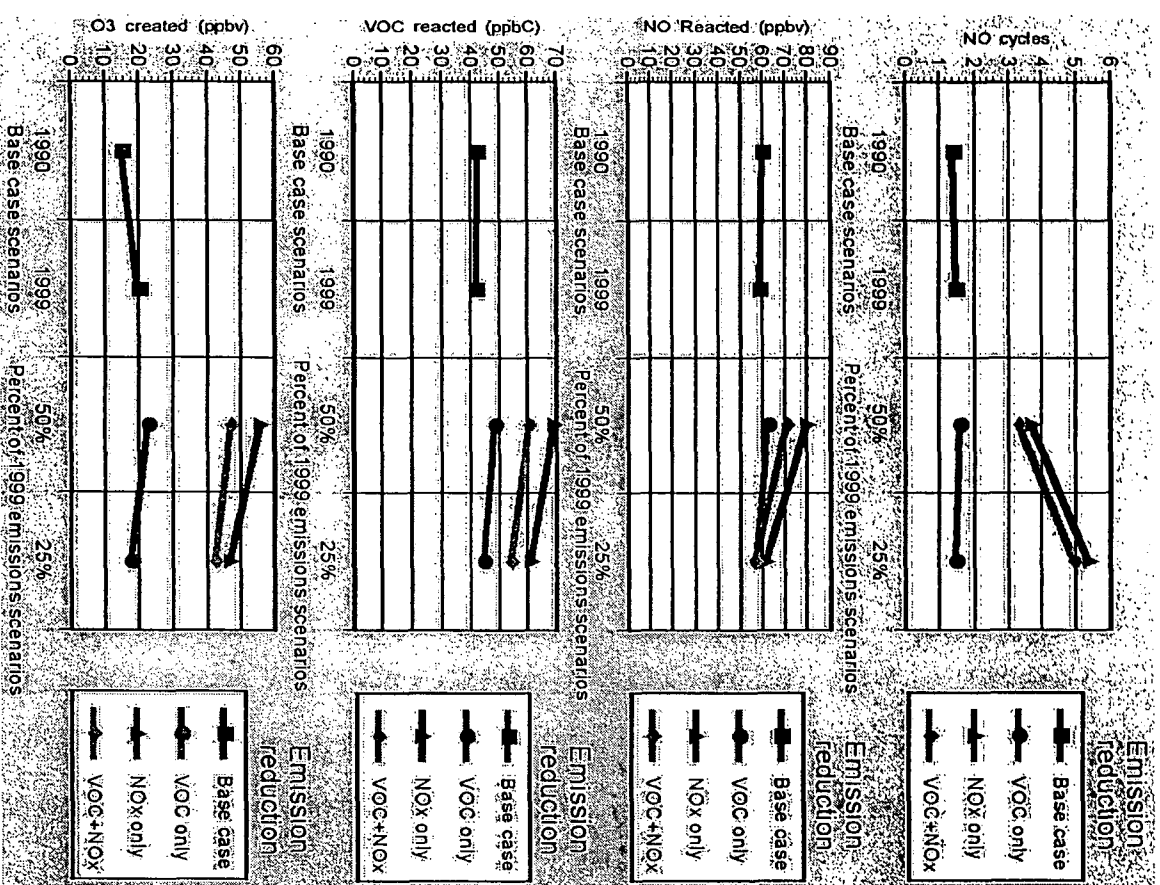
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# Process Analysis Results

- Useful elements of process analysis results
  - NO cycles (~ ozone produced per NO)
  - mass of NO reacted
  - mass of VOC reacted
  - ozone created
- Ozone production involves
  - radical initiation, propagation, and termination
  - NO recreated by photolysis of NO<sub>2</sub>



# Summary of key process analysis results for San Jose - August 5



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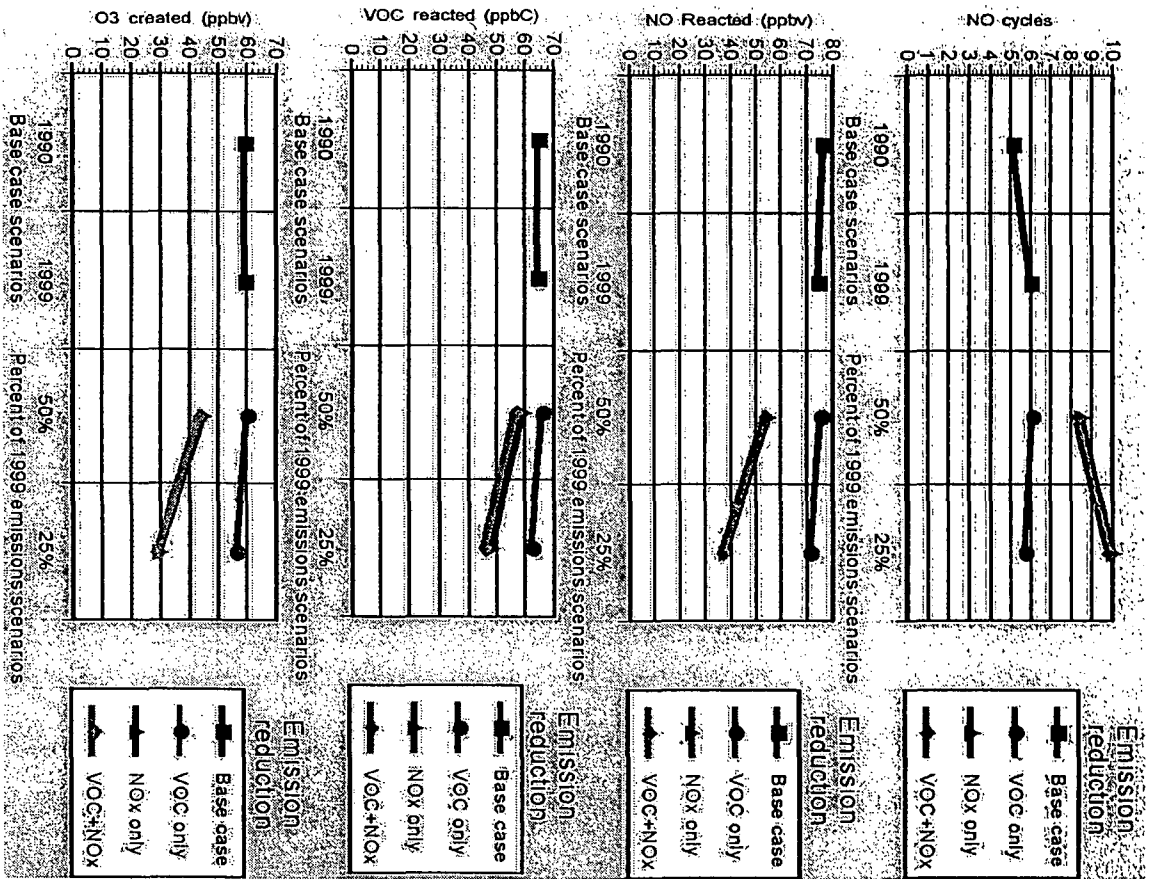


# Process Analysis Results for San Jose

- Lower precursor emissions in 1999 produce higher ozone relative to the levels formed in 1990
- Increased ozone forming efficiency in 1999
- 50 percent reduction in NO<sub>x</sub> emissions coupled with a 250 percent increase in NO cycles yields an increase in the mass of NO reacted...and ozone produced



# Summary of key process analysis results for Stockton - August 5



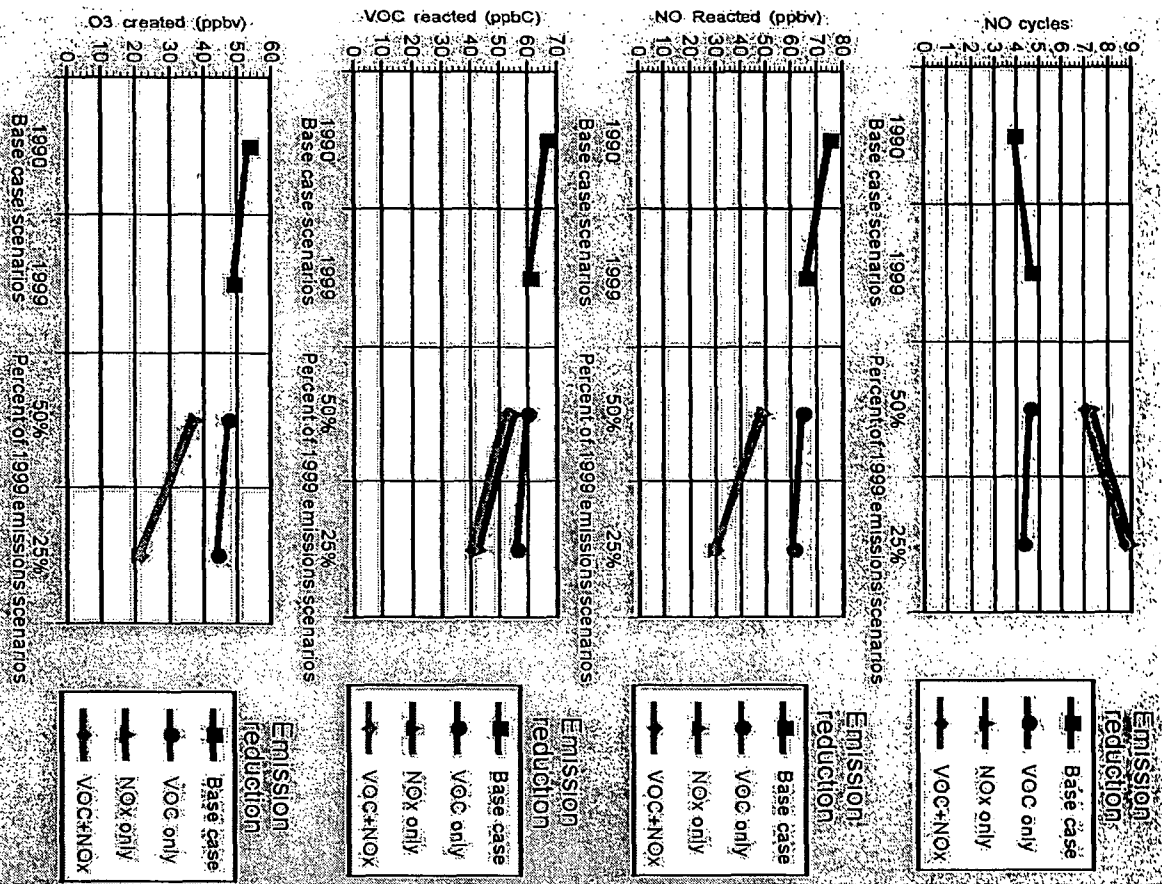
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# Process Analysis Results for Stockton

- Ozone produced in 1999 comparable to 1990
  - NO cycles increase, NO mass reacted decreases
- 50 percent NO<sub>x</sub> emissions scenario
  - 40 percent increase in NO cycles
  - net decrease in NO reacted
- 25 percent NO<sub>x</sub> emissions scenario
  - 100 percent increase in NO cycles
  - net decrease in NO reacted by 50 percent



# Summary of key process analysis results for Bakersfield - August 5



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# Process Analysis Results for Bakersfield

- Ozone in 1999 ~ 10-30 percent lower than 1990
  - total OH reacted is less in 1999
- 50 percent NO<sub>x</sub> emissions scenario
  - increases in NO cycles offset by decreases in NO reacted in proportions similar to Stockton
- 25 percent NO<sub>x</sub> emissions scenario
  - 100 percent increase in NO cycles
  - net decrease in NO reacted by 50 percent



# Summary of Process Analysis Results

- Reductions in NO<sub>x</sub> lowered 8-hour ozone concentrations but effectiveness offset by increases in NO cycles
- Substantial NO<sub>x</sub> emissions reductions required to reach 8-hour standard in Stockton and Bakersfield
- VOC reductions have little effect on either OH or NO cycles or the mass of VOC reacted



# Summary of Process Analysis Results

- Anthropogenic VOC reductions
  - effective in lowering peak 1-hour ozone levels in areas where anthropogenic emissions dominate biogenic sources
  - effectiveness limited in lowering peak 8-hour ozone due to contributions of biogenic VOC and anthropogenic CO emissions
- CO contribution to ozone produced significant when VOC and NO<sub>x</sub> emissions at 25 percent level



# Analyses of Ambient Ozone and Precursor Data in Central California

- Characterize trends, explain observed patterns, assess how patterns relate to modeling results
- Trends determined from annual statistics using t-tests of log-transformed data
- 4th highest 8-hour maximum, annual 1-hour maximum, and annual 1- and 8-hour maxima averaged over 21 days per year





# Analyses of Ambient Ozone and Precursor Data in Central California

- Average diurnal concentration profiles for 21 high-ozone days
- Data separated into
  - weekdays and weekends
  - 3- and 5-year time periods

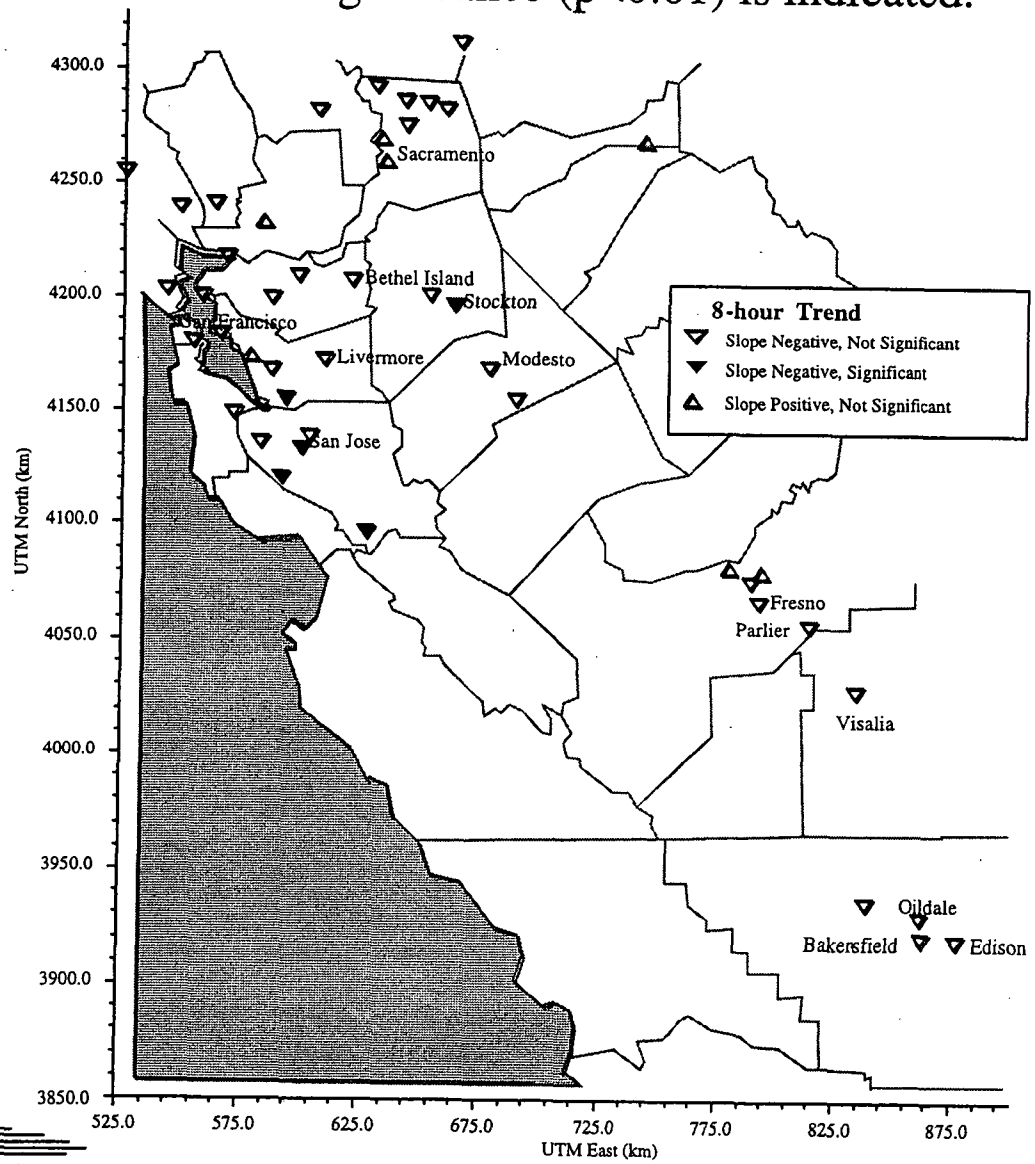


## Observed Ozone Trends

- 4th-highest maximum daily 8-hour ozone concentrations declined at most sites in central California
  - statistically significant ( $p < 0.01$ ) only at some sites in Bay Area and Stockton
- Annual 1-hour maxima also declined
  - statistically significant at more sites

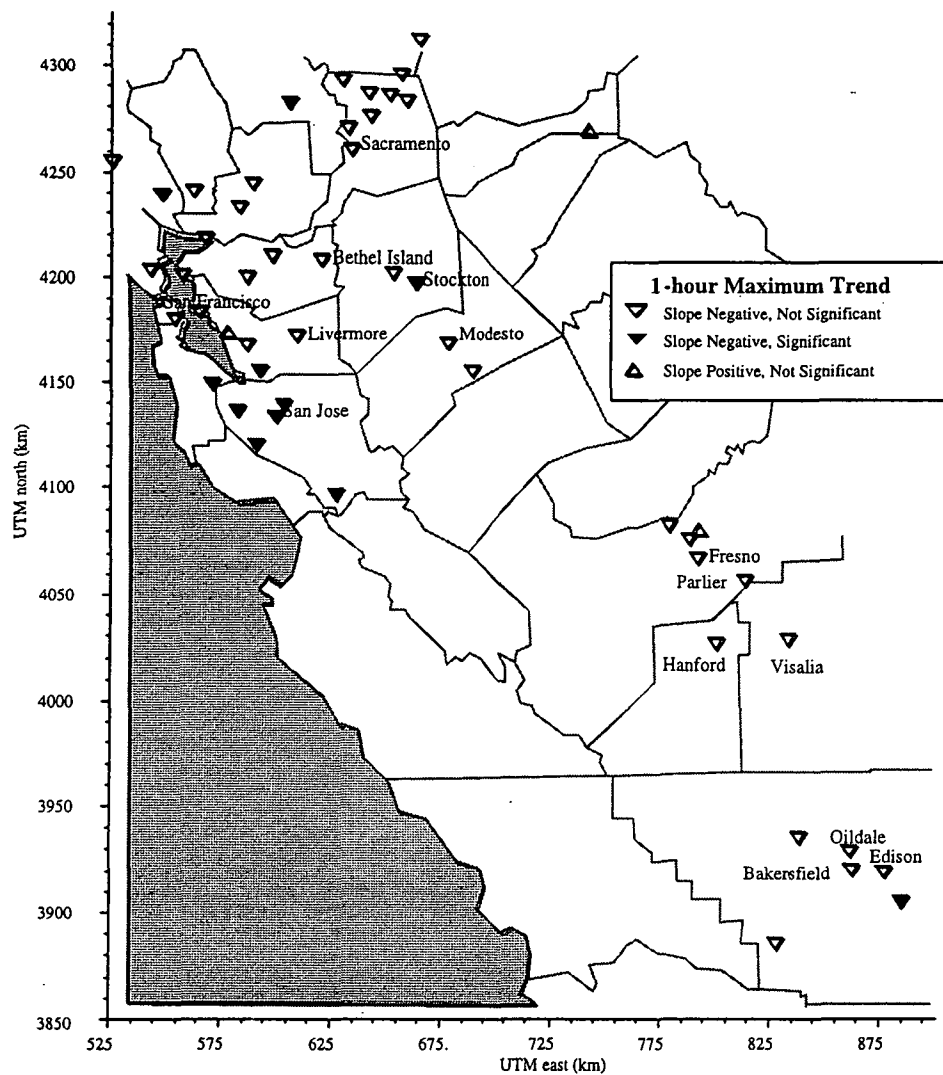


Trends in annual 4<sup>th</sup>-highest maximum daily 8-hour ozone concentration, 1980 through 2000. Statistical significance ( $p < 0.01$ ) is indicated.



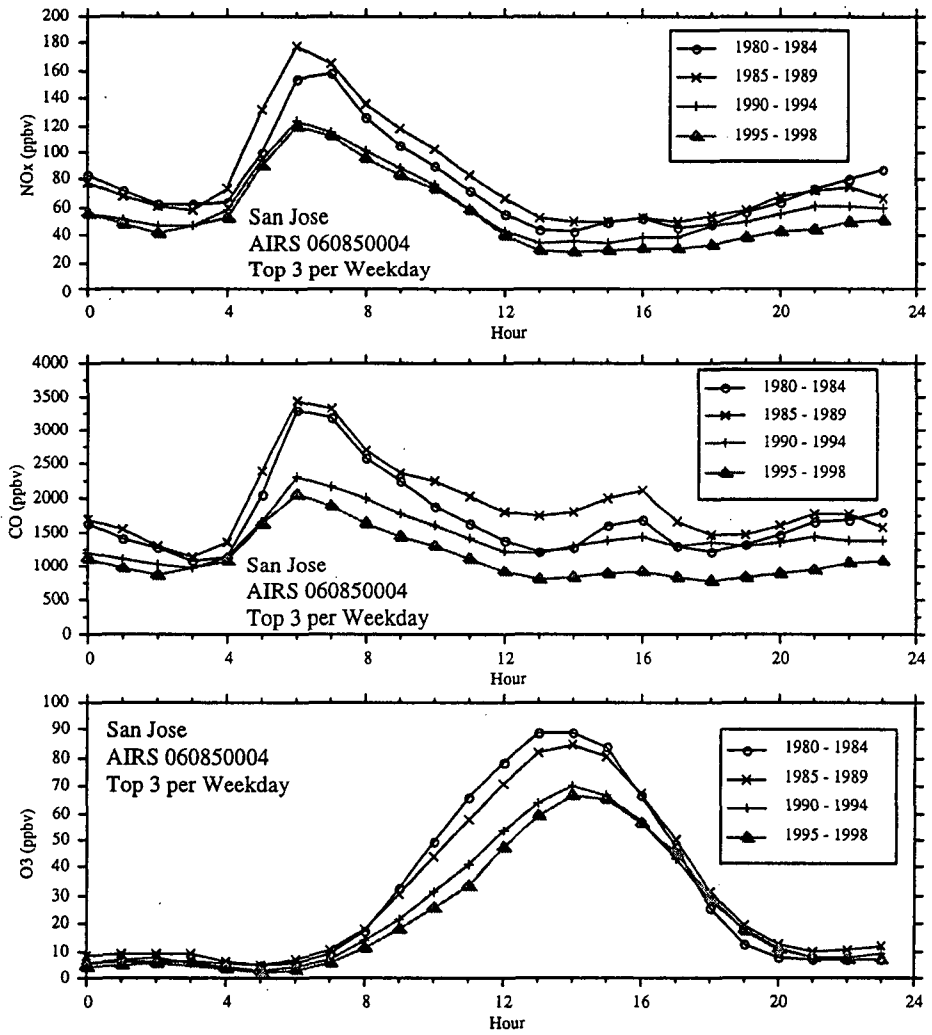
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### Trends in annual maximum daily 1-hour ozone concentration, 1980 through 2000. Statistical significance ( $p < 0.01$ ) is indicated.



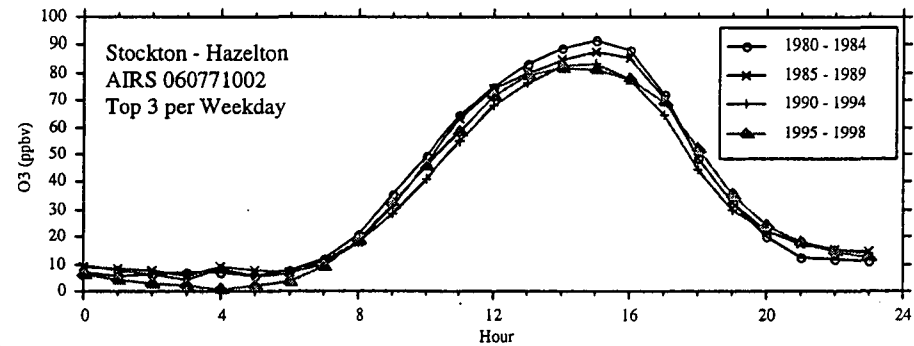
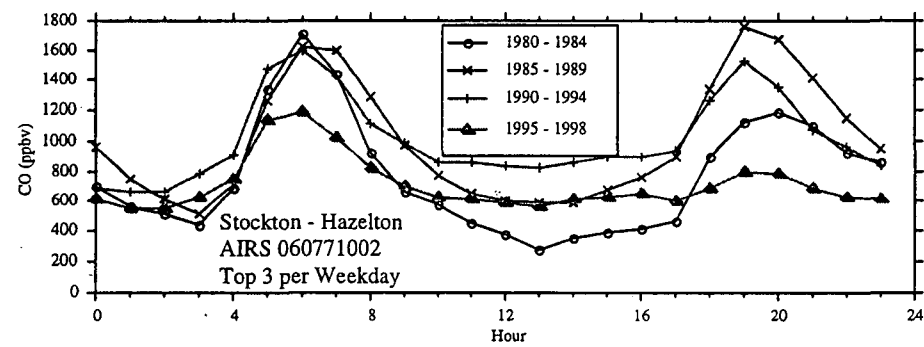
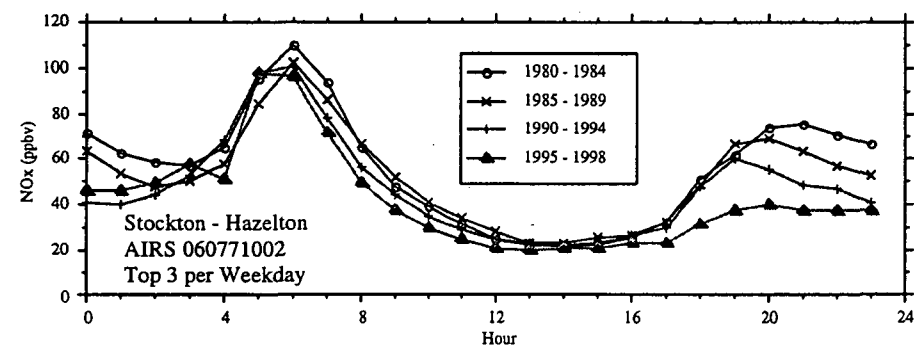
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# Diurnal patterns of ozone, NOx and CO at the San Jose 4th Street site



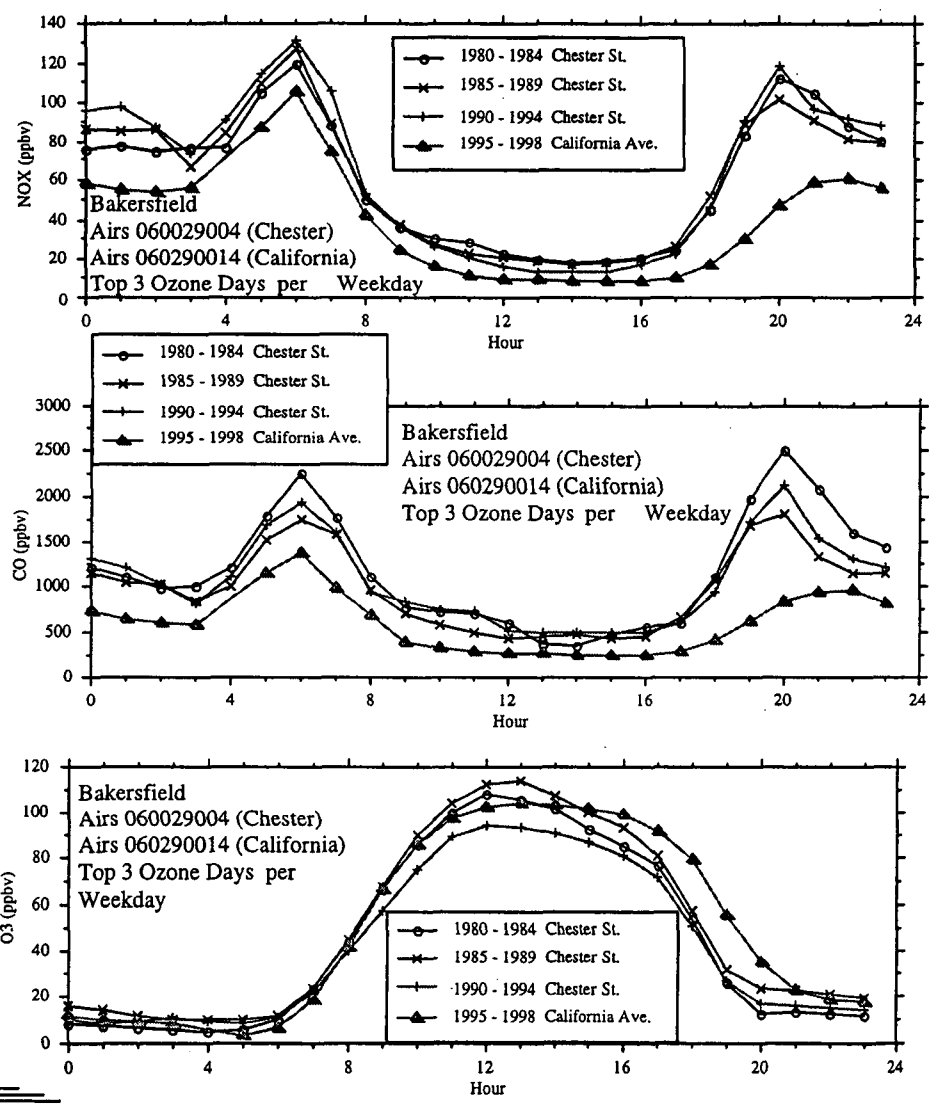
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# Diurnal patterns of ozone, NOx and CO at the Stockton site



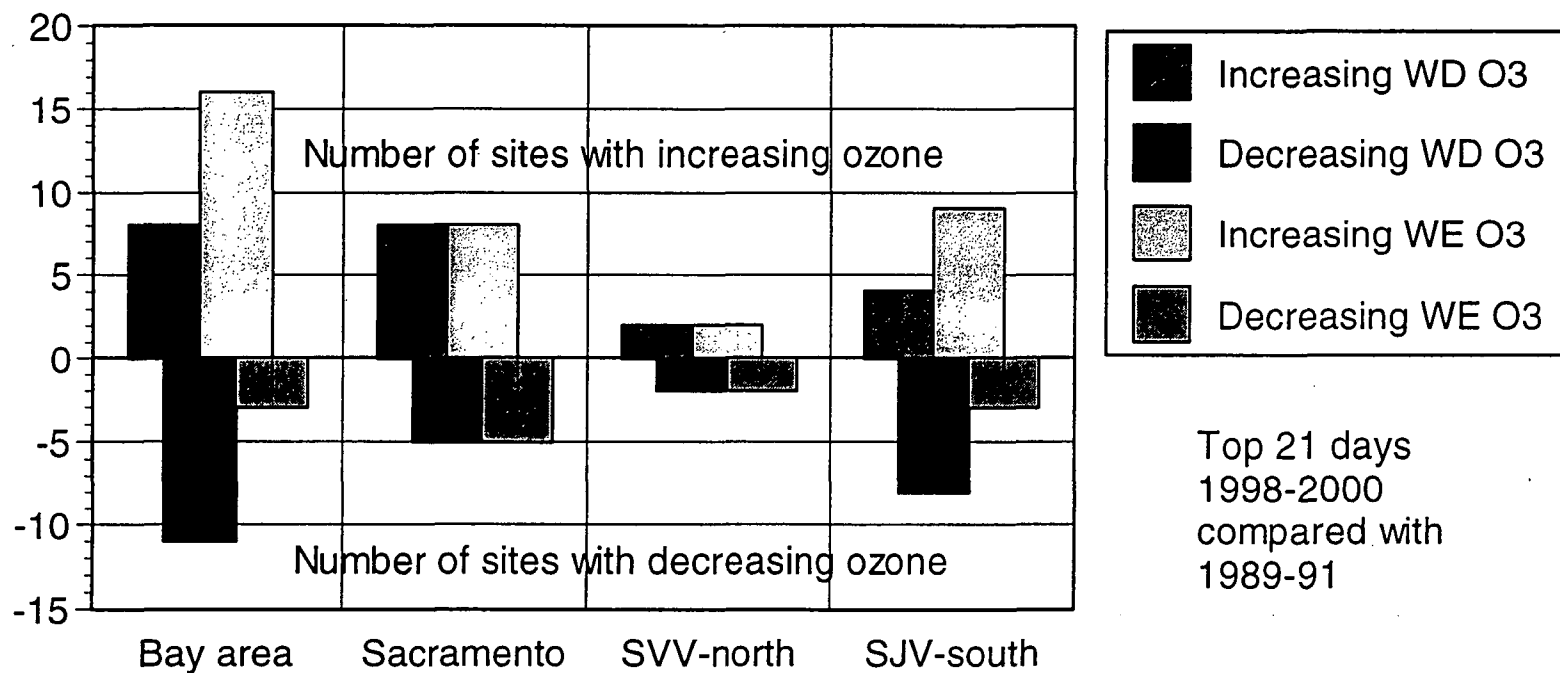
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# Diurnal patterns of ozone, NOx and CO at the Bakersfield sites



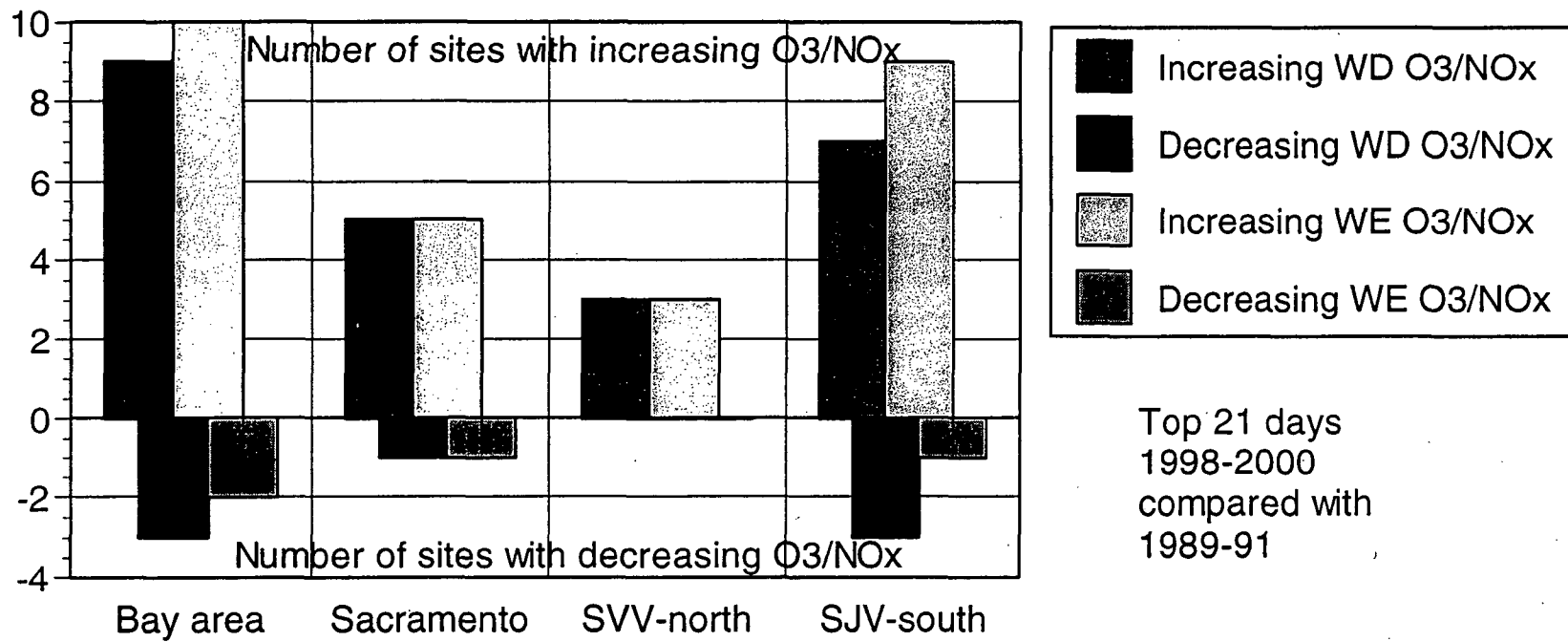
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Mean maximum hourly ozone on Top 21 days:  
 Comparable numbers of sites with increases and decreases

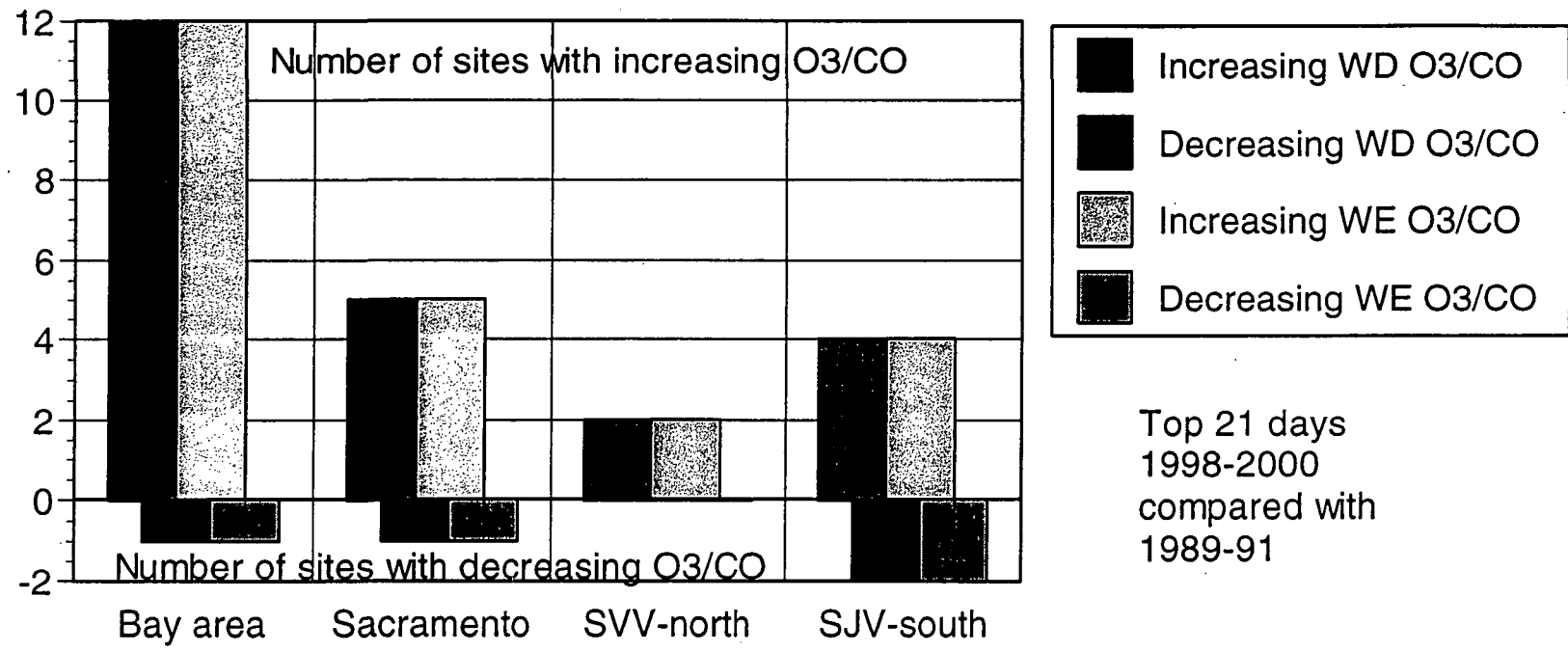




### Mean maximum hourly O3/NOx on Top 21 days: Many more sites with increases than decreases

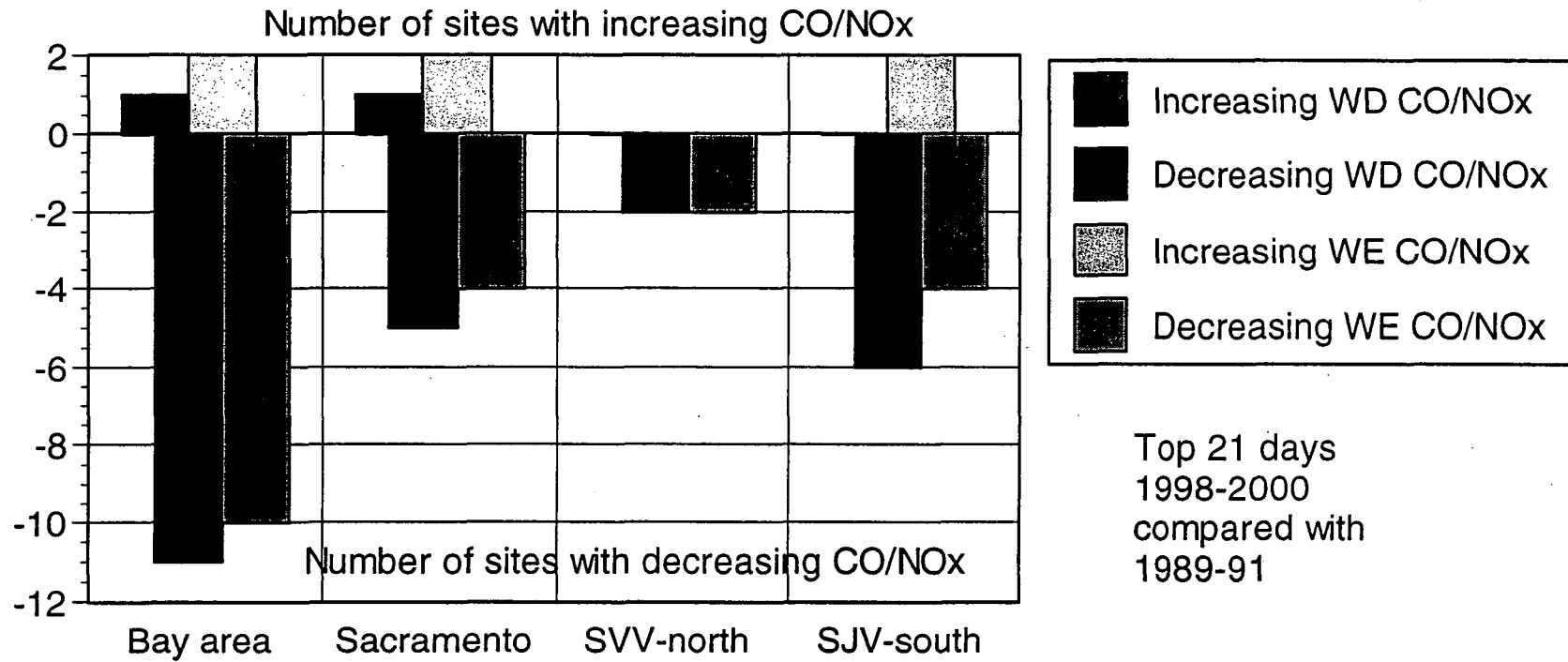


### Mean maximum hourly O3/CO on Top 21 days: Many more sites with increases than decreases



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### Mean maximum hourly CO/NOx on Top 21 days: Many more sites with decreases than increases



# Comparison of Modeling and Ambient Data Analysis Results

- Limitations of modeling results
  - uncertainties in biogenic emissions estimates
  - unclear whether ozone response for modeling period is representative of other days when moderate to relatively high 8-hour ozone concentrations occur



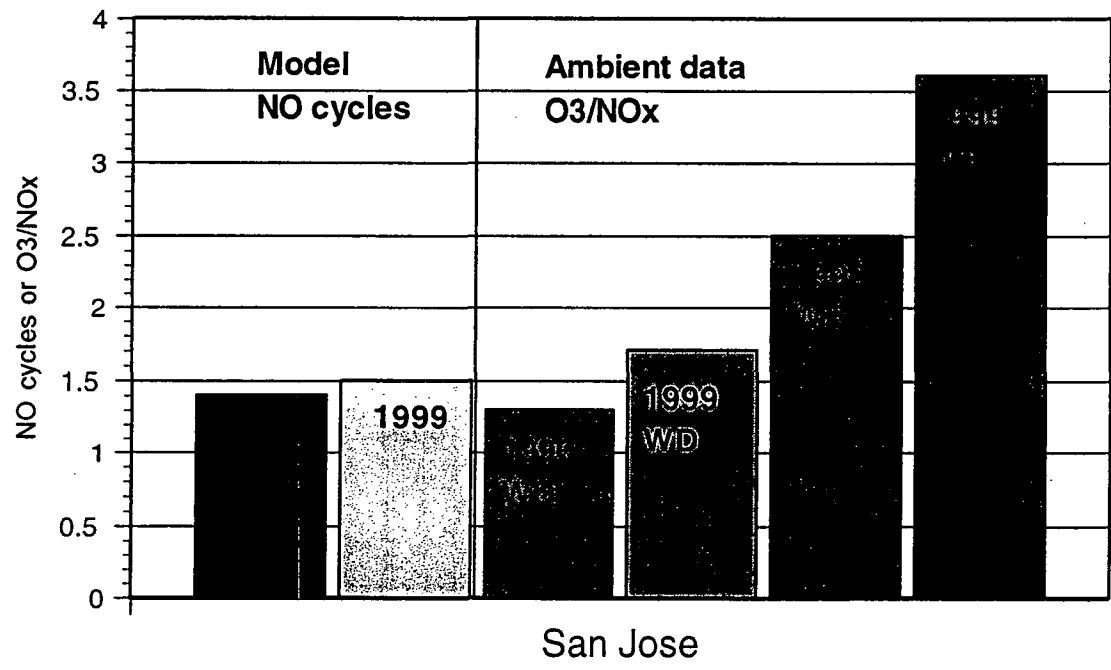
# Comparison of Modeling and Ambient Data Analysis Results

- Consistency of modeling and ambient data analysis results
  - both indicate modest changes in ozone levels over the period from 1990 to 1999
  - observed changes in ambient NO<sub>x</sub> and CO corroborate the ~30 percent reduction in NO<sub>x</sub> and VOC emissions
  - both indicate consistent increases in model NO cycles and ambient O<sub>3</sub>/NO<sub>x</sub> ratios



Consistent increases in:

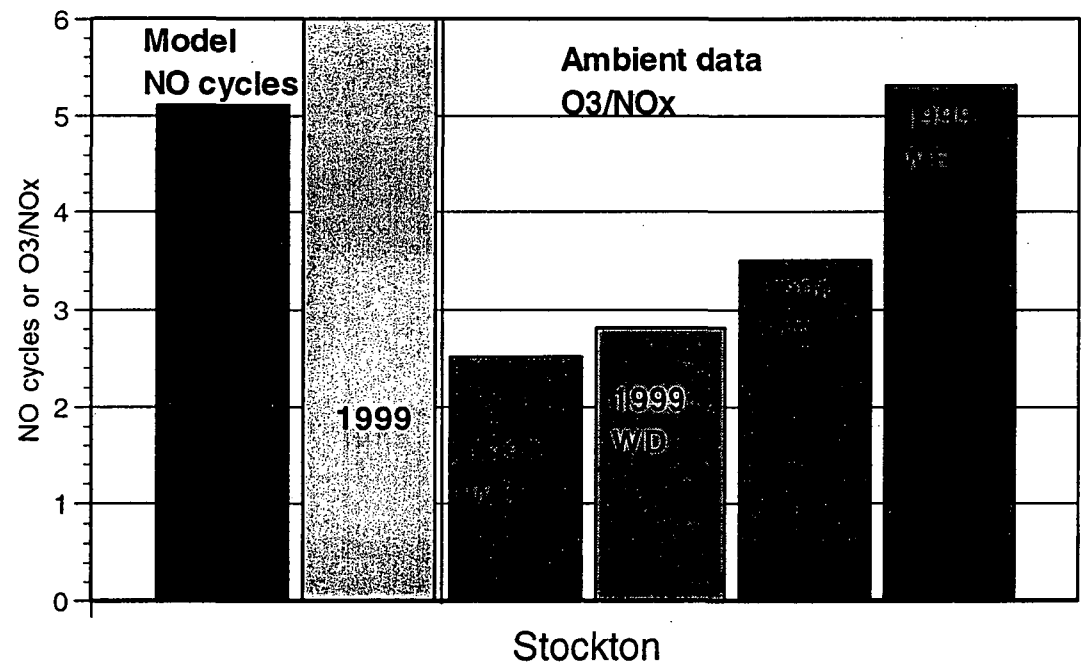
- > model-predicted NO cycles from 1990 to 1999
- > ambient ozone/NOx ratios, 1989-91 and 1998-00



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Consistent increases in:

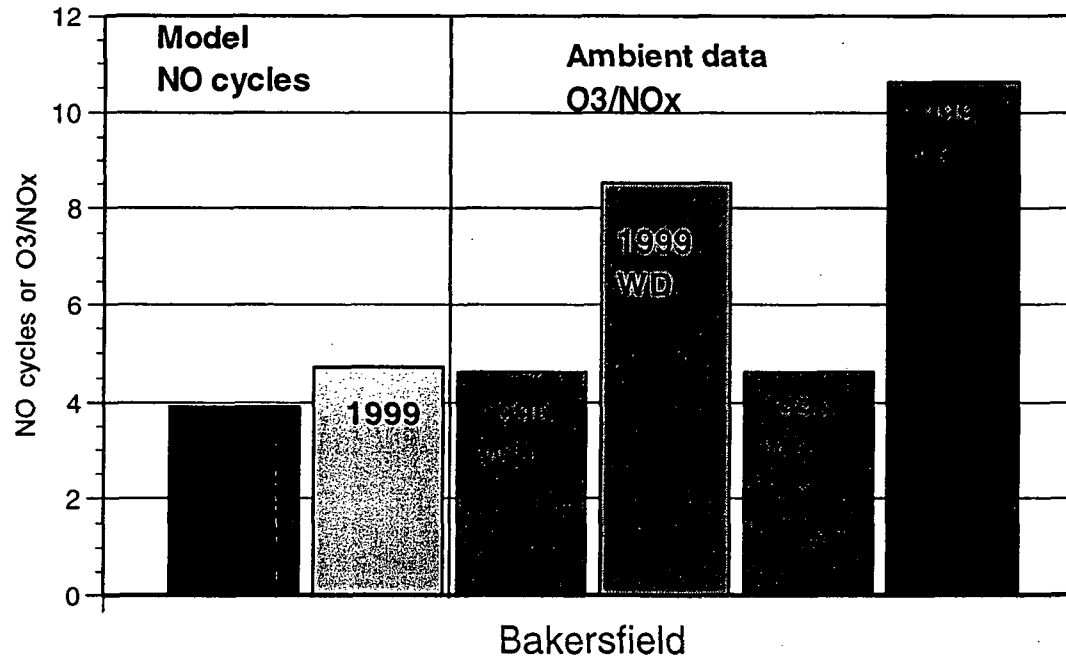
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Consistent increases in:

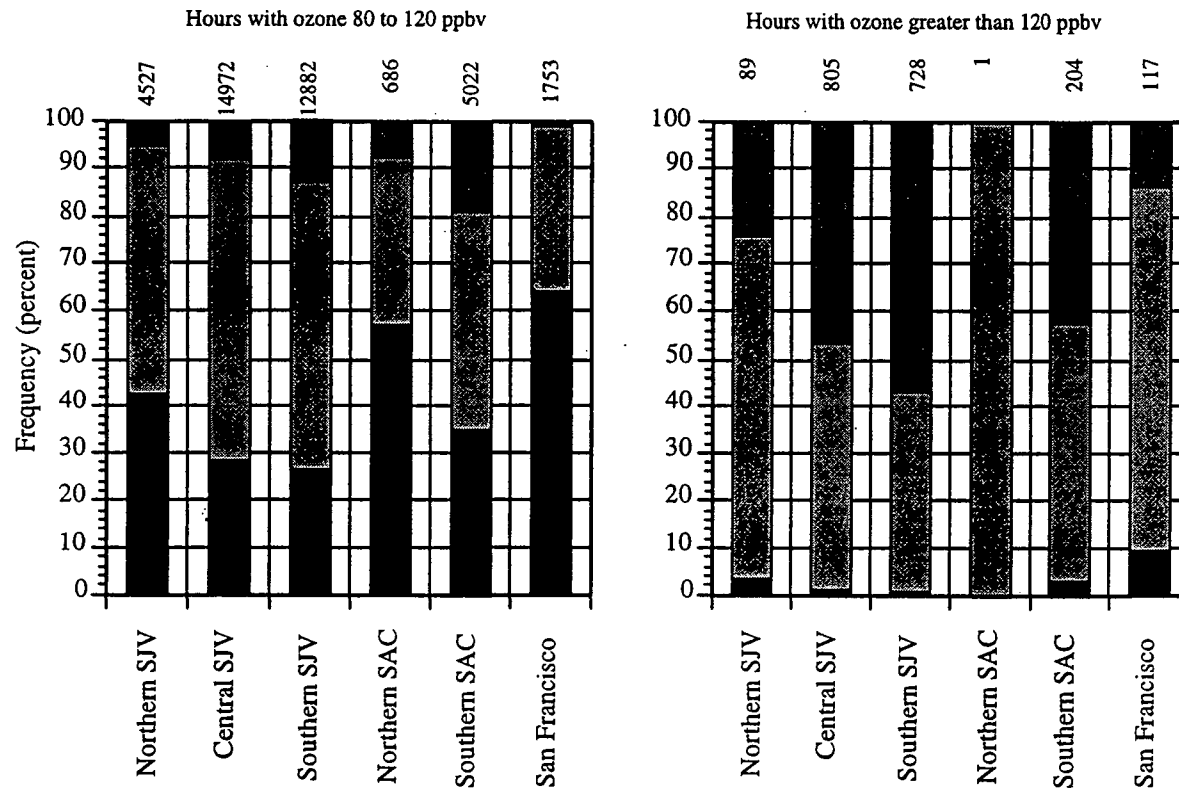
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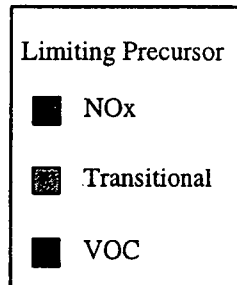
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Frequency of occurrence (percent of hours) of limiting ozone precursor in central California areas for hours with ozone concentrations of 80-120 ppbv (left panel) and hours exceeding 120 ppbv (right panel). March through October, 1994-2000.

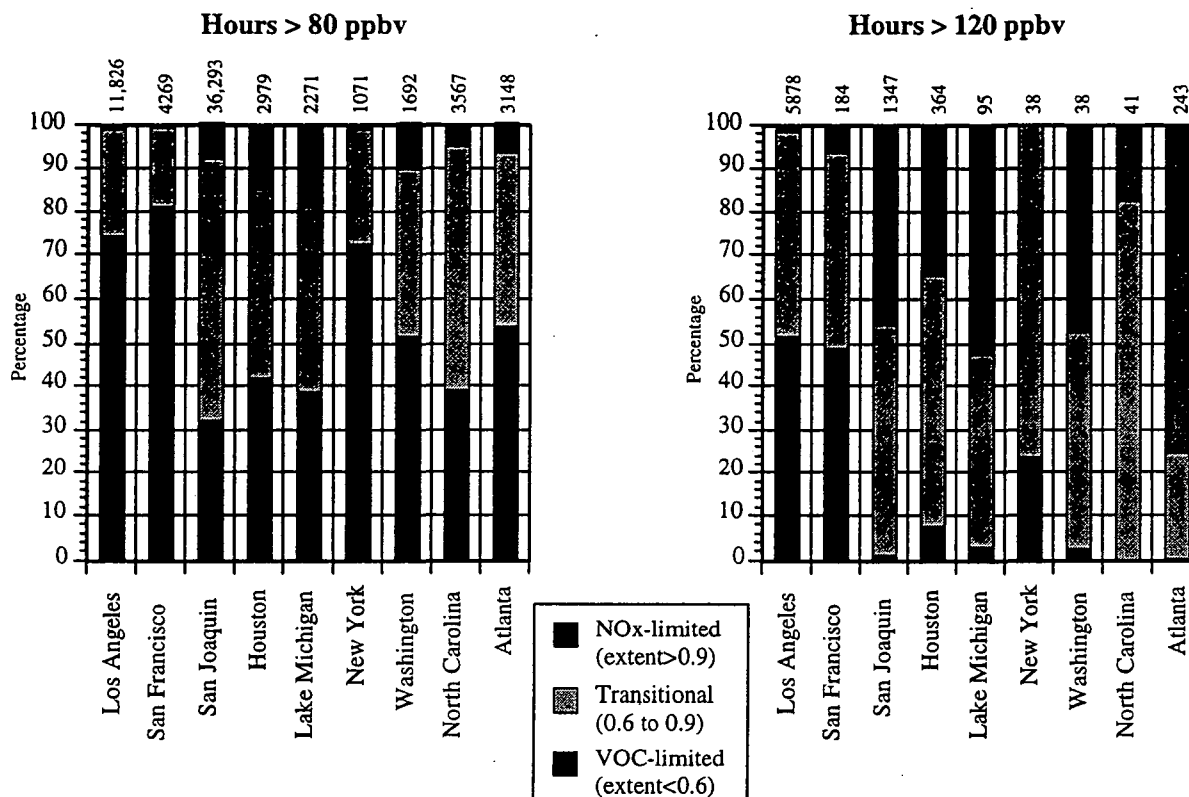


All days March - October  
1994 - 2000



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## FREQUENCY OF VOC-LIMITED, TRANSITIONAL, AND NO<sub>x</sub>-LIMITED HOURS AT ALL MONITORS

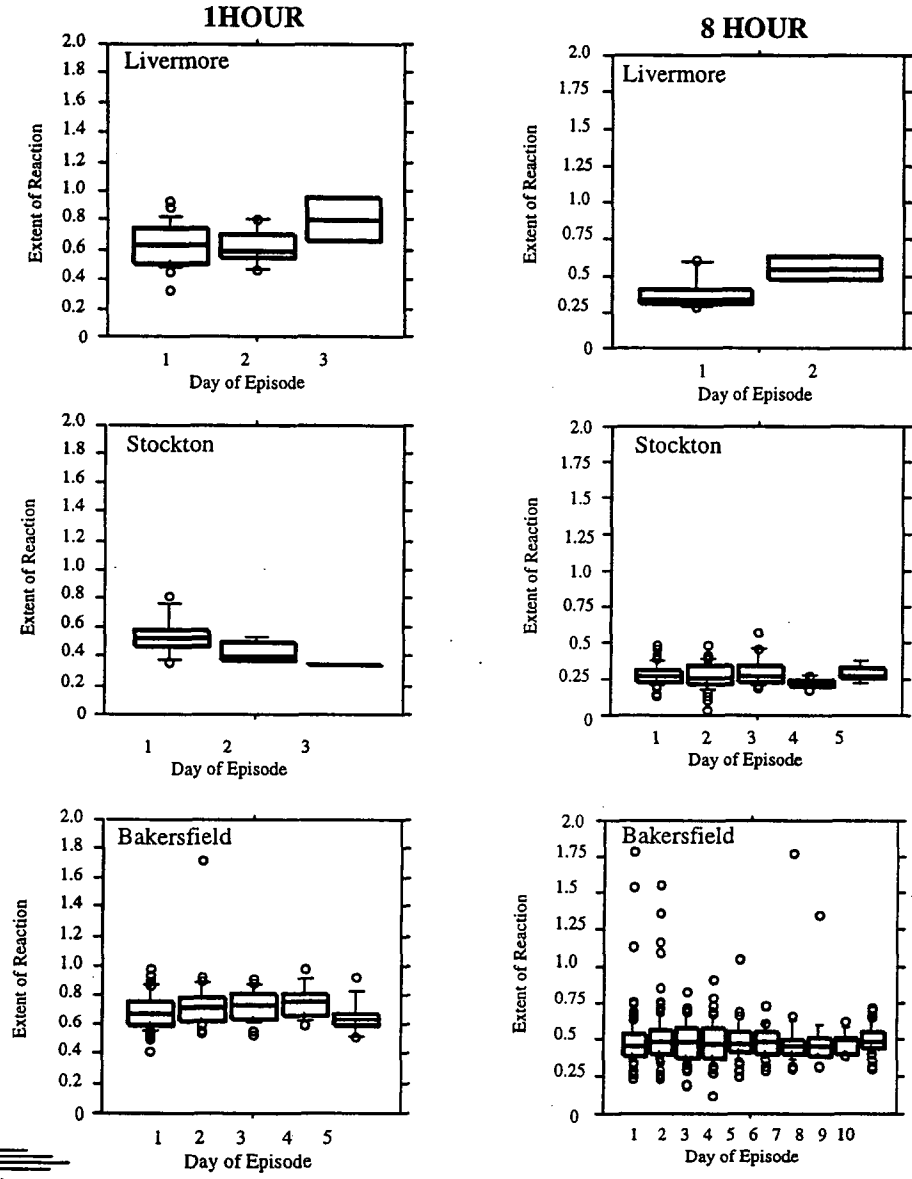


Central California	1991-98
Texas	1993-99
Southern California	1994-97
Atlanta	1994-99
Northeast and mid-Atlantic	1994-99
Southern Lake Michigan area	1994-98

In all areas, frequency of NO<sub>x</sub> limited hours is greater for hours with ozone > 120 ppbv (right) than for hours with ozone > 80 ppbv (left).



# Extent of reaction during 1-hour and 8-hour episode days in 1994-2000 versus sequence of days within an episode



# Conclusions

- Various VOC and NO<sub>x</sub> emissions reductions effective in reducing peak 1-hour ozone levels
- VOC reductions have modest impact on peak 8-hour ozone concentrations
- Anthropogenic NO<sub>x</sub> emissions must be reduced by 90 percent to reach the 8-hour ozone standard



# Conclusions

- Anthropogenic VOC reductions ineffective because biogenic VOC, less reactive VOC, and CO continue to produce ozone
- Effectiveness of NO<sub>x</sub> reductions offset by an increase in ozone produced per NO
- Such NO<sub>x</sub> reductions may increase ozone levels in some areas
- These results call into question the technical feasibility of attaining the 8-hour ozone standard



# Recommendations for Further Study

- Conduct data analyses and modeling in another area to assess consistency of findings with those obtained in central California
  - northeastern U.S. using CMAQ



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